

# **Studies of the Navy-ARPA Chemical Laser (NACL) Exhaust**

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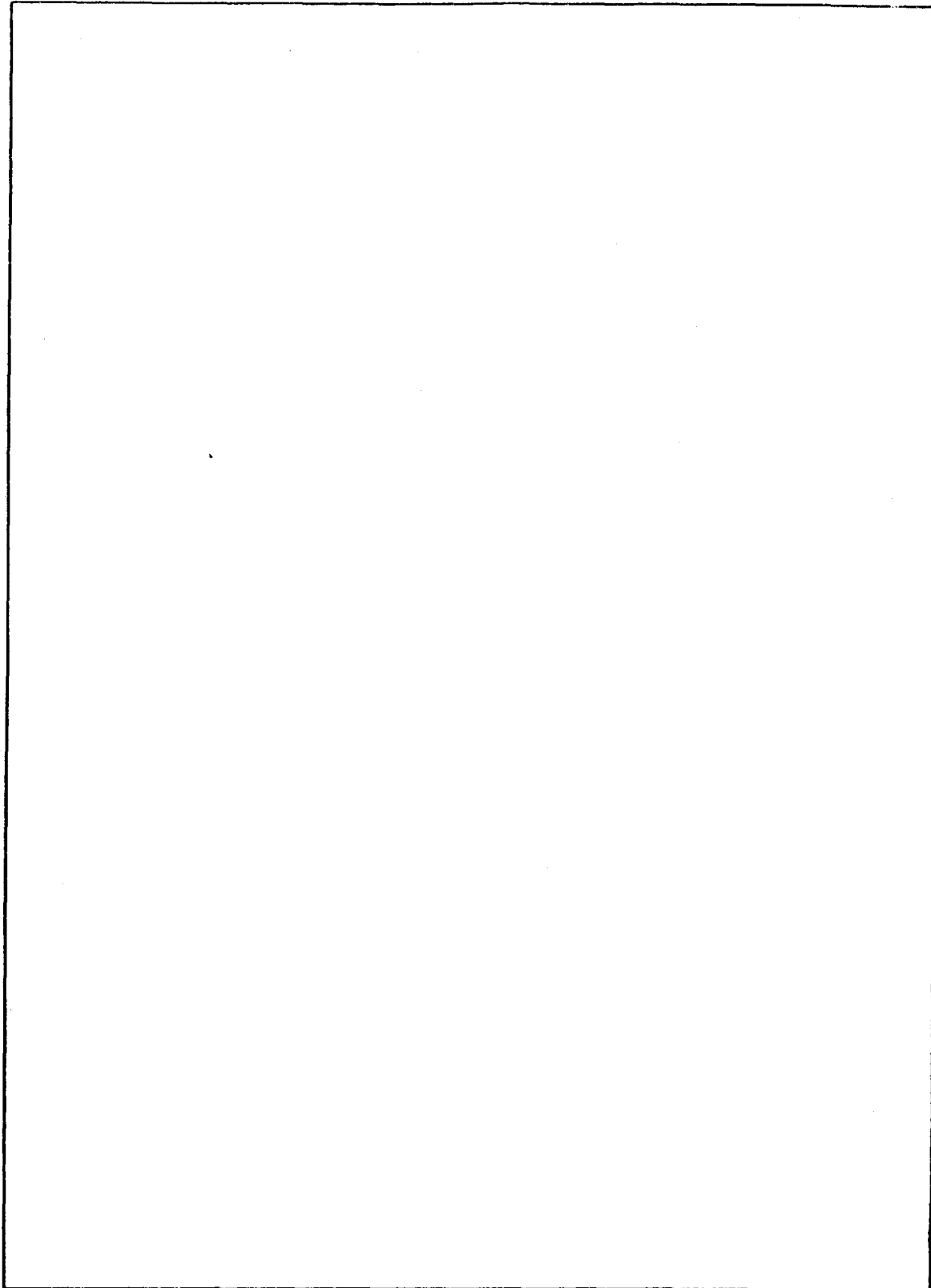


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# STUDIES OF THE NAVY-ARPA CHEMICAL LASER (NACL) EXHAUST

## INTRODUCTION

The Navy is interested in knowing the composition of the exhaust of chemical laser systems which could be used aboard ships [1]. TRW has tested the Navy-ARPA Chemical Laser (NACL), which can serve as a potential model for a shipborne system. During the course of NACL operation, relatively large quantities of the laser combustor fuel (ethylene,  $C_2H_4$ ), cavity fuel (deuterium,  $D_2$ ), combustor oxidizers (fluorine,  $F_2$ , and nitrogen trifluoride,  $NF_3$ ), helium diluent, and nitrogen pressurization/purge gases are used. The reaction of the fuel and oxidizers within the laser system results in the formation of large quantities of hydrogen fluoride and deuterium fluoride (HF and DF) and, presumably, significant quantities of other fluorine compounds. Substances which may be present in the exhaust include  $CF_4$ ,  $COF_2$ , DF,  $F_2$ , He, HF,  $N_2$ ,  $NF_3$ ,  $N_2F_2$ , NO,  $N_2O$ , and  $OF_2$ . Exhaust products generated by NACL operation are removed by a steam-driven ejector pumping system.

Determination of laser exhaust constituents will facilitate definition of actual and potential health hazards, determination of maximum permissible concentrations of exhaust constituents from land-based and shipboard laser systems, determination of efficiency of the present NACL exhaust scrubber system, better definition of performance requirements for efficient shipboard laser scrubber systems, and assessment of the environmental impact resulting from the NACL exhaust.

This study addresses the two major unknowns concerning the NACL exhaust, the identities of minor chemical species which may exist as vapors in the exhaust immediately after the laser and the concentration of particulate matter formed in the laser. To resolve these questions the following experimental approach was adopted. To determine the nature of the chemical species present, gas samples upstream from the scrubber of the NACL were analyzed directly by an on-line mass spectrometer interfaced to a programmable calculator. Downstream sampling was not employed because dilution by large quantities of steam would significantly lessen the sensitivity of the measurements and might be detrimental to the mass spectrometer. Additionally, it should be possible to infer what reactions the chemical species undergo in the pumping.

For the determination of particulate matter, all particles were trapped on filters placed both upstream and downstream from the pumps. Downstream sampling is straightforward because it is done at atmospheric pressure, but upstream sampling required external pumping, as is discussed later. After being filtered, the sampled gases were passed through scrubbers to trap hydrofluoric acid.

## EXPERIMENTAL ANALYSES

### Gas Analysis

The sampling procedure used for gas analyses was designed to analyze the laser effluent in situ during the firing of the laser and thereby provide the most representative data about the composition of the gas. The analysis system is depicted schematically in Fig. 1. A sampling line was connected to a port about 15 m (50 ft) downstream from the laser on the 2-m (6-ft) diameter pipe through which the NACL is pumped. The gas samples were pumped through a 9.5-mm (3/8-in.) o.d. stainless-steel tube inserted to the center of the pipe. The tube was connected to a stainless-steel solenoid valve about 0.3 m (1 ft) outside of the pipe; the valve was opened only during sampling. The other side of the solenoid valve was connected to the mass-spectrometer-assembly leak valve with 2.5 m (8 ft) of 9.5-mm (3/8-in.) i.d. Teflon tubing. The sample flows through the leak valve and is pumped by a 25-l/min vacuum pump.

As shown in Fig. 1, a flow restrictor with a conductance of  $100 \text{ cm}^3/\text{min}$  is placed between the mass-spectrometer assembly and the pump so that the principal pressure drop is across the flow restrictor. For example, if the pressure in the 2-m (6-ft) pipe is 2.7 kPa (20 torr) and the pressure at the pump inlet is 0.7 kPa (5 torr), the pressure in the mass-spectrometer leak valve would be 2.1 to 2.4 kPa (16 to 18 torr). Thus, the pressure in the leak valve will correspond within 20% to that in the pipe. Since the pressure in the pipe is known, the leak valve can be adjusted to a leak rate that will give the best mass-spectrometer performance. Without the flow restrictor, the pressure in the leak valve would be much more sensitive to tubing configuration between the pipe inlet and the leak valve.

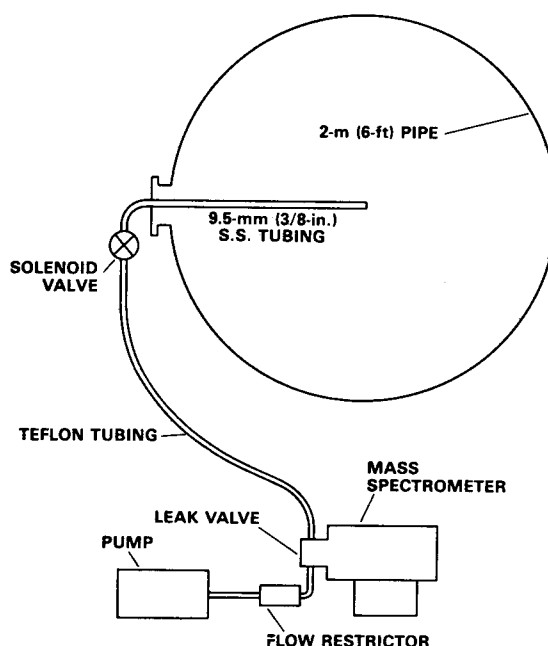


Fig. 1 - Schematic of on-line mass spectrometer to NACL pump duct

More details of the mass-spectrometer assembly are depicted in Fig. 2. As the sample passes through the leak valve (Varian Model 951), a small amount of the sample leaks into the vacuum housing containing the mass spectrometer (UTI Model 100C) where it is analyzed. The spectrometer assembly is pumped by a 20-l/s ion pump. During sampling the pressure in the vacuum housing increases to about  $270 \mu\text{Pa}$  ( $2 \mu\text{torr}$ ) from its background pressure of less than  $1 \mu\text{Pa}$  ( $0.01 \mu\text{torr}$ ). The transit time for the sample from entry into the 9.5-mm (3/8-in.) stainless-steel tube to mass analysis is less than 1 s.

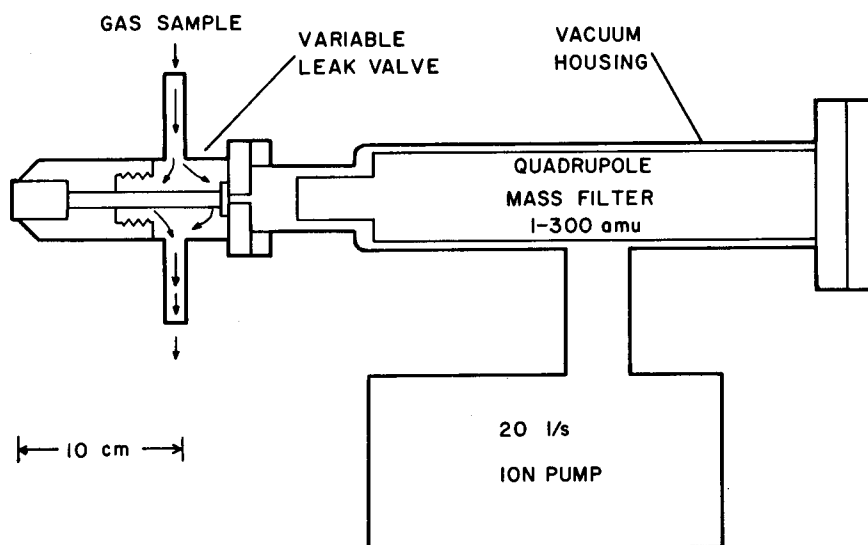


Fig. 2 — Arrangement of mass spectrometer, leak valve, ion pump, and vacuum housing

The electronics which control the mass spectrometer are interfaced to a Hewlett Packard Model 9825A programmable calculator, which controls the mass setting and gain of the mass spectrometer, measures signals from the mass spectrometer, and records the pressure in the vacuum housing (based upon ion-pump current). With this system, a mass spectrum over the mass range 2 to 200 can be obtained and stored in 5 s. This includes changing the gain of the mass spectrometer in order that mass peaks which differ in intensity by a factor of  $10^6$  can be measured.

During the firing of the laser, the following procedure was used to gather the data. At about  $T = 0$ , a signal was sent from the control center to actuate the solenoid valve. This signal also started the programmable calculator that scanned the mass spectrometer, and every 5 s a mass spectrum was obtained and stored. At termination of the firing, usually about  $T + 30$  s, the signal from the control center was turned off, closing the solenoid valve. The final mass spectrum was acquired and the system shut down. Thus, 7 or 8 mass spectra could be obtained during the above-described firing sequence. In addition to each mass spectrum, signals corresponding to the pressure in the vacuum chamber and the time at the start of each spectrum were recorded.



For preliminary experiments the mass-spectrometer assembly was not directly connected via the laser [2]. Instead, three evacuated 500 cm<sup>3</sup> stainless-steel cylinders were connected via the solenoid valve to the laser exhaust pipe. During the operation of the laser the valve was opened to sample the gas from the laser. Each cylinder was then removed and connected to a gas-circulating loop which included the leak valve on the mass spectrometer; the loop was evacuated and sealed, the valve on the cylinder opened, and a circulating pump started. The leak valve on the mass spectrometer was opened and mass spectra taken. This experimental arrangement, shown in Fig. 3, was designed to allow the mass spectrometer to be adjusted to obtain the best possible data when actual NACL samples were observed. If necessary, the programming of the calculator which controls the mass spectrometer could be modified.

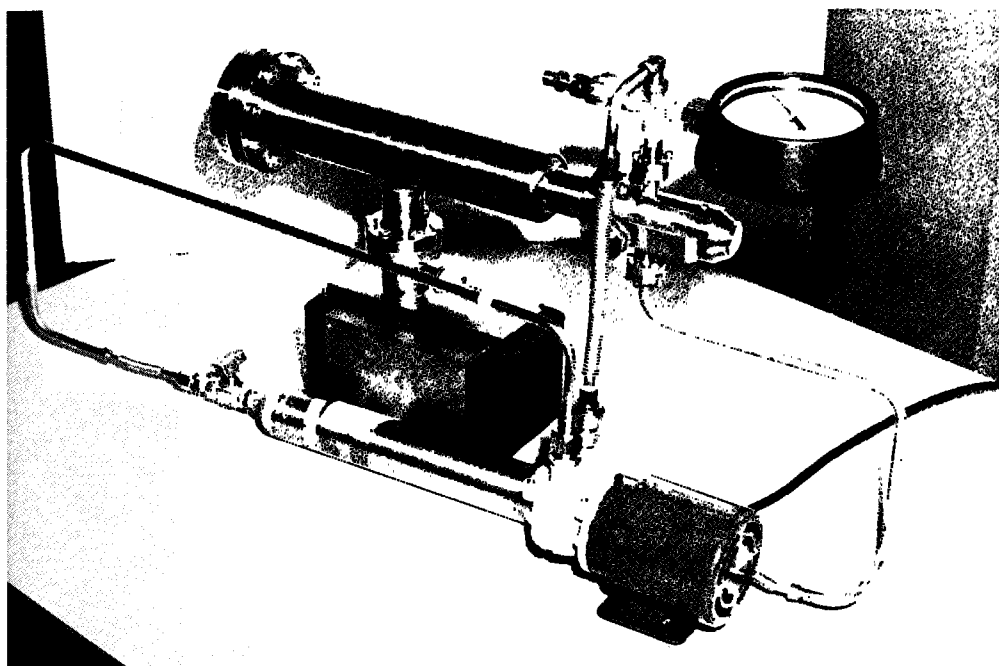


Fig. 3 – Photograph of arrangement used for analyzing the sampling cylinders

### Particulate and Fluoride Gas Analysis (Wet Chemical)

Particulate and fluoride gas samples collected from the main duct about 15-m (50-ft) downstream of the laser and from the duct exhaust downstream of the steam ejector were brought back to NRL for examination and analysis. The particulate samples were collected on polyvinyl chloride or fibrous glass filter papers. The fluoride gas samples were collected in gas absorption tubes packed with granular lithium hydroxide (LiOH). LiOH reacts with hydrogen or deuterium fluoride via the following reaction:



Samples from the main duct were collected by probes, one at the duct centerline and one near the wall, each with its end curved 90° and oriented to face upstream. The probes were mounted in openings in the duct wall by means of pipe plugs adapted with O-ring seals. Each sampling system consisted of a probe, a solenoid valve, a filter holder, and a two-stage LiOH gas absorption tube, connected in that order. Two stages of LiOH were used to assure efficiency of absorption. Each sampling system was connected by rubber vacuum hose to a 60-l vacuum ballast tank and a 150-l/min vacuum pump.

The sampling procedure was to have the vacuum pump operating to maintain a vacuum in the ballast tanks and then to open the solenoid valve to draw a sample. Typical pressure in the duct during laser firing was about 5.3 kPa (40 torr); the net flow into the evacuated sampling system was about 6 l-atm/min. Sample volumes were measured with a gas meter connected to the vacuum-pump exhaust. Samples were collected with this system from  $T + 5$  s to the end of the run (before the duct was vented).

Downstream, at the exhaust exit, the two filter holders were held by clamps so that straight probe tubes extended about 0.6 m (2 ft) into the open end of the exhaust duct. These filter holders were each followed in line by a two-stage LiOH absorber to collect fluoride gas samples. Suction for these samplers was provided by diaphragm pumps (Gelman Little Giant, 36.8-l/min capacity) and was controlled by solenoid valves at the pump inlets. The measured net flow through these samplers was 30 l/min.

There was an accumulation of dust and other debris along the inside wall of the main duct, particularly where drifts had formed against obstructions or in stagnant areas. Samples of this dust were withdrawn from the duct with a suction pump during one of the shutdown periods. These samples were brought back to NRL for examination and analysis.

## RESULTS

### Gas Analysis (Mass Spectrometric)

The laser was sampled initially during the period from 20 to 27 June 1977, but because only one firing on 20 June was not aborted, a limited amount of qualitative data were obtained. The first sampling, on the morning of June 20, used evacuated cylinders as described in the previous section. Duplicate samplers were set up, each having three cylinders. The solenoid valve was opened between  $T + 10$  s and  $T + 15$  s. All the cylinders were analyzed but none had the expected reaction products. There was a large amount of air (estimated to be about 1 kPa [10 torr]), which had leaked into the cylinders. Apparently the leak was through the solenoid valve. The effect was aggravated by the 6-h delay between clearing the laser site and firing. In addition to air, HF and Freon 113 were observed. Freon 113 is a common cleaning solvent used with the laser. Several other attempts to obtain more samples were fruitless due to the laser firing being aborted near  $T = 0$ . It was decided to go directly to on-line sampling in order to obtain some data during the visit to the test site.

The mass spectrometer was connected on-line, as described in the previous section. The laser firing on 24 June was the only one which produced any useful data for this setup, and this was marginal. Sampling was begun at  $T + 4$  s, the laser shut down at  $T + 6$  s, and sampling terminated at  $T + 10$  s. The mass spectrometer took two spectra during this period, but since

each spectrum takes about 5 s, neither spectrum was acquired under steady-state conditions. Consequently, the spectra could be analyzed only in the most qualitative manner. Peaks corresponding to all the feed gases were observed, along with peaks corresponding to HF, DF, CF<sub>4</sub>, and HD. All other attempts during this time to obtain on-line data were unsuccessful due to aborted laser firings. On 27 June, several malfunctions occurred in our equipment. Since the NACL was to be shut down for several days, we returned to NRL to examine our data and to repair equipment.

The laser was sampled again on 9 September 1977. Two successful sampling runs were performed. The first laser firing (VL2-170)\* began about 12:15 and lasted 30 s, the second (VL2-171)\* at 18:30 and lasted 17 s. The following day we experienced equipment failure. Since a large amount of data had been obtained already, it was felt that it would be most productive to return to NRL to analyze the data and to repair the equipment. As discussed below, analysis of the data showed the sampling of both runs to be successful. At this time an additional trip to the NACL to perform mass spectrometric sampling could not be justified because of the low probability of obtaining additional information which would not duplicate that already in hand.

#### **Analysis of Data from Runs VL2-170 and VL2-171**

During run VL2-170 eight mass spectra were obtained; during run VL2-171 six mass spectra were obtained. Table 1 lists the times and the pressures in the mass-spectrometer vacuum system for these spectra. All of the mass-spectrometric data are given in the appendix. Between the two runs the mass-spectrometer leak was opened more to increase sensitivity. A pressure of about 270  $\mu$ Pa (2.0  $\mu$ torr) is the maximum for best instrument performance. As can be seen from the pressure readings in Table 1, for run VL2-170 spectra 4, 5, and 6 should be most representative. For run VL2-171 spectra 4 and 5 should be most representative. Although for this run spectrum 5 was not completed until  $T + 19$ , the data should be valid. The last second for data gathering is used to record the data on a cassette. Thus the actual data for this run were acquired only during  $T + 15.2$  to  $T + 18.2$ . As noted in Table 1 the D<sub>2</sub> was shut off at 17.4 s. It is felt that the 0.8 s between this time and the gathering of the final data point would not affect the data, because of delays due to the time required for gas flows. Additionally, during this time the system was scanning between mass peaks 70 and 150 at the highest sensitivity setting. As discussed below, virtually nothing is observed in this region of the mass spectrum.

Before we discuss conclusions based upon the data, it is necessary to comment upon the interpretation of the mass spectra. A mass spectrometer analyzes the intensity of ions produced when the sample gas in it is ionized. Upon ionization most molecules fragment into a variety of ions. The characteristic intensity of these fragments or ionic pieces of the molecule can serve as a fingerprint to detect the presence of a particular molecule. Fragmentation presents a difficulty when one analyzes mixtures, because different compounds often produce the same fragment ions upon ionization. Thus, the usable sensitivity of a mass spectrometer to a given species depends often upon which fragment ion can be observed without inference, rather than upon the absolute sensitivity of the mass spectrometer. Other factors such as ionization cross section, mass discrimination, and mass-dependent multiplier gain also affect the overall sensitivity. Table 2 lists various species and the fragment ions used to calculate their concentrations.

\*These numbers were used by TRW as designators for the runs.

Table 1 — Pressures and Times for Mass Spectra from  
Runs VL2-170 and VL2-171

Spectrum	Start Time (s)	Pressure		Comments
		$\mu\text{Pa}$	$\mu\text{torr}$	
Run VL2-170				
1	$T + 0.0$	1	0.01	$D_2$ on at $T + 4.0$
2	$T + 4.1$	63	0.47	
3	$T + 8.7$	84	0.63	
4	$T + 13.3$	84	0.63	
5	$T + 17.8$	84	0.63	
6	$T + 22.4$	84	0.63	
7	$T + 26.8$	84	0.63	$D_2$ off at $T + 29.4$
8	$T + 31.1$	84	0.63	
Run VL2-171				
1	$T - 4.0$	4	0.03	$D_2$ on at $T + 4.0$
2	$T - 0.2$	110	0.83	
3	$T + 5.0$	200	1.50	
4	$T + 10.2$	200	1.50	
5	$T + 15.2$	200	1.50	$D_2$ off at $T + 17.4$
6	$T + 20.3$	200	1.50	

Table 2 — Fragmentation Values Used

Species	Fragment	Mass	Fraction of Total
He	$\text{He}^+$	4	1.00
HF	$\text{HF}^+$	20	0.50
DF	$\text{DF}^+$	21	0.50
$\text{N}_2$	$\text{N}_2^+$	28	0.95
$\text{NF}_3$	$\text{NF}_2^+$	52	0.60
	$\text{NF}_3^+$	71	0.10
$\text{CF}_4$	$\text{CF}_3^+$	69	0.90
$\text{H}_2\text{O}$	$\text{H}_2\text{O}^+$	18	0.70
HDO	$\text{HDO}^+$	19	0.70
$\text{D}_2\text{O}$	$\text{D}_2\text{O}^+$	20	0.70

An example of the use of mass-spectral data is the calculation of the concentration of the HF detected. It is seen from Table 2 that both HF and D<sub>2</sub>O produce an ion at mass 20. The intensity due to D<sub>2</sub>O can be calculated based upon the amount of H<sub>2</sub>O and HDO present. For example, in spectrum 6, Run VL2-170, the intensities at masses 18, 19, and 20 are 682, 211, and 34, respectively. From these numbers one calculates a ratio of H/D of 8/1, therefore the ratio of H<sub>2</sub>O to D<sub>2</sub>O is 64/1. Thus, the intensity at mass 20 due to D<sub>2</sub>O is  $682/64 = 11$ . It follows then that the HF intensity is  $34 - 11 = 23$ . Comparing this to the intensity due to N<sub>2</sub> at mass 28 and dividing each intensity by its respective fraction from Table 2, one finds the HF to be 4.7% of the nitrogen. Correspondingly, the DF is about 0.09% of the N<sub>2</sub>.

The above data imply two things. First, based upon gases flowing into the laser the HF + DF intensity should be similar to the N<sub>2</sub> intensity. Therefore, a large fraction of the HF and DF is lost to the walls of the sampling system. Similar behavior was observed when HF/N<sub>2</sub>/He mixtures were sampled in the laboratory. It is believed that the HF is adsorbed on the walls of the leak valve at the leak surface and on the walls of the high vacuum system. The second conclusion is that the HF and DF are rapidly exchanging hydrogen with water, producing the large amount of HDO.

By the use of calculations similar to those above, concentrations can be calculated for various species. Since there is a large amount of uncertainty in the data, concentration estimates are probably good to within a factor of 3, except for HF and DF, which are lost to the walls of the sampling system. Table 3 lists all peaks from spectrum 4, Run VL2-171, with an intensity greater than 1.0 and the species which primarily contribute to each peak. Depending upon fragmentation, an intensity of 1.0 would correspond to a gas concentration of 0.05% to 0.3% of the N<sub>2</sub> concentration. Table 4 lists the various species tabulated in Table 3 and their probable sources.

An example of the use of the data to calculate the maximum concentration of a toxic compound is presented for COF<sub>2</sub>. The known mass spectrum of COF<sub>2</sub> has a peak at mass 47, which is about 0.5 of the sum of all its ion intensities [3]. From the data for Run VL2-171, the intensity of mass 47 increases to about 0.4 then levels off at 0.2. Using a value of 2000 for the N<sub>2</sub> intensity, one calculates from the data of Table 2 that COF<sub>2</sub> at a maximum would be

$$(100\%)(0.4/0.5)/(2000/0.95) = 0.04\% \quad (2)$$

of the N<sub>2</sub> intensity. A similar calculation could be performed for the NF<sub>3</sub> oxidizer. From the spectra one can observe a rapid increase in the intensity of mass 52 (see Table 2), which disappears in later spectra.

In Table 4 the only fluorine compounds listed are HF, DF, and CF<sub>4</sub>. If we assume that any toxic compound from the laser would be fluorinated, then there is no toxic material detected other than HF and DF. Since the limit of detectability is approximately 0.3% of the N<sub>2</sub> concentration, and, as discussed below, the HF and DF concentration is about equal to the N<sub>2</sub> concentration, an unknown product would have to be more than 300 times as toxic as HF to be equally dangerous. Therefore, the principal toxicological hazard from the NACL is from HF and DF.

Table 3 — Species Giving Major Contributions  
to Various Masses  
(Spectrum 4, Run VL2-171)

Mass	Intensity	Species
2	1238	H <sub>2</sub>
3	662	HD
4	11572	He, D <sub>2</sub>
16	74	H <sub>2</sub> O, HDO
17	517	H <sub>2</sub> O, HDO
18	2000	H <sub>2</sub> O
19	417	HDO
20	47	HF, D <sub>2</sub> O
21	1.5	DF
25	2.4	C <sub>2</sub> H <sub>4</sub>
26	2.9	C <sub>2</sub> H <sub>4</sub>
27	12	C <sub>2</sub> H <sub>4</sub>
28	2021	N <sub>2</sub>
29	17	N <sub>2</sub>
30	8	NO
31	8	CF <sub>4</sub>
32	3	O <sub>2</sub>
36	1	HCl
40	48	Ar
44	17	CO <sub>2</sub>
50	22	CF <sub>4</sub>
69	211	CF <sub>4</sub>

Table 4 — Species Sources

Species	Major Source
H <sub>2</sub> , HD	H <sub>2</sub> O, HDO, and D <sub>2</sub> O decomposition in mass spectrometer ion pump.
D <sub>2</sub>	Fuel and HDO and D <sub>2</sub> O decomposition in the mass spectrometer ion pump and walls of sampling line inside the duct
HDO, D <sub>2</sub> O	DF exchange with H <sub>2</sub> O
HF, DF	Laser product
C <sub>2</sub> H <sub>4</sub>	Laser fuel
N <sub>2</sub>	N <sub>2</sub> window and laser product
NO	Reaction of N <sub>2</sub> and H <sub>2</sub> O in the mass spectrometer ion pump.
CF <sub>4</sub>	Laser product
O <sub>2</sub>	Background
HCl	Cl impurity in F <sub>2</sub>
Ar	Impurity in N <sub>2</sub>
CO <sub>2</sub>	Product of CF <sub>4</sub> and H <sub>2</sub> O decomposition in the ion pump.

### Fluoride Analysis (Wet Chemical)

Operation of the NACL during the August 1977 tests (Runs VL2-154 and 155) was sporadic and subject to many variations of conditions. During the December 1977 tests (Runs VL2-247 to 250) operation was more regular, subject to interruption only by weather or other nontechnical factors. Hence, data collected in December are more representative of normal conditions than are data collected in August.

The HF and DF gases collected in the granular LiOH absorbers were analyzed by means of a fluoride-specific ion meter (Orion Research Corporation, Model 801A, fitted with a fluoride electrode). The LiOH was dissolved in a minimum quantity of 12N hydrochloric acid and the resulting solution adjusted to a pH of 5 with a proprietary buffer solution prepared by Orion Research Corporation. The fluoride content of the resulting solution was measured with the specific ion meter. From this value and the volume of gas sample drawn the fluoride concentration in the gas was calculated. This concentration is shown in Tables 5 and 6 as concentration at ambient atmospheric pressure and temperature. For the steam-exhaust samples this is the actual concentration being emitted. For the duct samples it is the concentration to be expected if the duct were vented to the atmosphere without scrubbing or dilution with steam.

Table 5 — Concentration of Gaseous Fluoride ( $F^-$ )\*  
in NACL Duct Before Scrubber (August, 1977)

NACL Sample Position	Wt. F <sup>-</sup> in Sample (mg)			Volume of Gas Sampled (liters, atmospheric temperature and pressure)	Concentration of F <sup>-</sup> in Gas (mg/l, atmospheric temperature and pressure)
	Stage 1	Stage 2	Total (1 + 2)		
Run VL2-154, Aug. 3					
Duct Center	13.0 ± 0.3	0.02 ± 0.01	13.0 ± 0.3	0.18	72 ± 2
Duct Wall	6.6 ± 0.2	4.00 ± 0.30	10.6 ± 0.3	0.18	59 ± 2
Run VL2-155, Aug. 4					
Duct Center	22.6 ± 7.5	3.10 ± 0.20	26.0 ± 8.0	0.24	104 ± 30
Duct Wall	7.9 ± 0.2	4.50 ± 0.20	12.4 ± 0.2	0.24	52 ± 1

\*HF equivalent is  $F^- \times 1.053$ ; DF equivalent is  $F^- \times 1.105$ .

Table 6 — Concentration of Gaseous Fluoride ( $F^-$ )\*  
in Duct and Exhaust (December 1977)

NACL Sample Position	Wt. F <sup>-</sup> in Sample (mg)			Volume of Gas Sampled (liters, atmospheric temperature and pressure)	Concentration of F <sup>-</sup> in Gas (mg/l, atmospheric temperature and pressure)
	Stage 1	Stage 2	Total (1 + 2)		
Run VL2-247					
Exhaust 1	0.049	---	0.049	6.13	0.008
Exhaust 2	0.027	---	0.027	6.13	0.004
Run VL2-248					
Duct (long)	0.038	0.011	0.049	0.325	0.152
Duct (short)	0.026	0.003	0.029	0.325	0.088
Exhaust 1	0.024	---	0.024	3.83	0.006
Exhaust 2	0.031	---	0.031	3.83	0.008
Run VL2-249					
Exhaust 1	1.71	(1 and 2	1.71	4.6	0.37
Exhaust 2	0.855	combined)	0.855	4.6	0.19
Run VL2-250					
Duct (long)	1.735	0.039	1.774	0.49	3.6
Duct (short)	1.78	0.338	2.12	0.49	4.3
Exhaust 1	1.71	(1 and 2	1.71	4.98	0.34
Exhaust 2	2.85	combined)	2.85	4.98	0.56

\*HF equivalent is  $F^- \times 1.053$ ; DF equivalent is  $F^- \times 1.105$ .



As can be seen from the data, for some runs the efficiency of the LiOH absorption was quite good and on others it was marginal. The efficiency of absorption can be determined by observing the ratio of the fluoride ion measured in the first and second stages. For example, in Run VL2-250 the fluoride in stage 2 is less than 20% of that in stage 1. This calculation was not possible in the exhaust side as the large quantity of steam caused the two stages to partially dissolve and run together. Thus the fluoride-ion concentration for the exhaust side of the NACL is reported as a combined value.

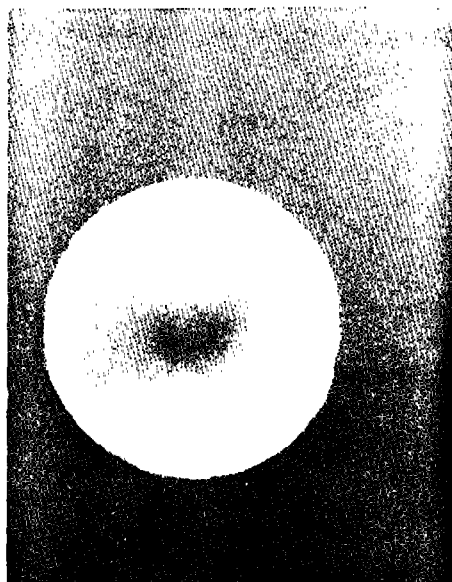
The fluoride concentrations in the duct for the August 1977 tests (Runs VL2-154 and VL2-155) averaged 66 and 77 mg/l. These values correspond to 86000 and 98000 ppm gas volume, respectively. There was no evidence of acid-insoluble residue that might be suspected to be carbon (soot). In the December tests the sampling solenoid valve apparently did not open in runs VL2-247 and VL2-248. Hence, the fluoride concentrations for these runs are very low and are therefore questionable. The exhaust sample for Run VL2-249 was valid and gave a concentration of 0.273 mg/l or 353 ppm on a volume basis. The data for Run VL2-250 are valid, having samples from the duct and exhaust simultaneously. Fluoride concentration in the duct averaged 3.90 mg/l or 5038 ppm, and that in the exhaust averaged 0.453 mg/l or 574 ppm. The data from Run VL2-250 thus show a scrubber efficiency of 30% for removing fluoride from the laser exhaust if the steam flow used for pumping was six times the duct gas flow.

### Particulate Analysis

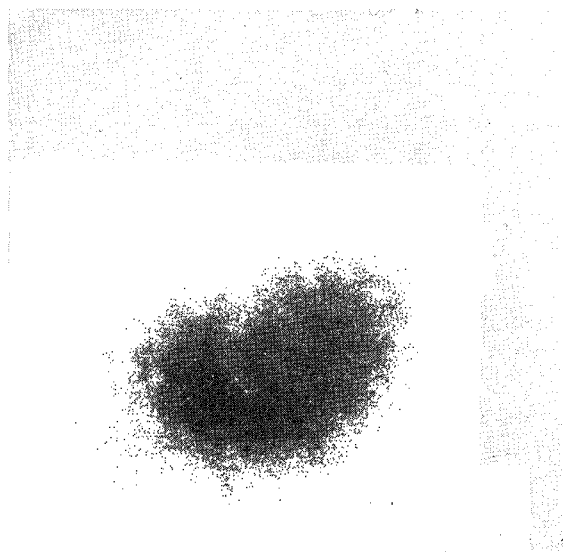
The particulate samples collected on filters were examined by visual, optical microscope, and electron microscope methods. Visual examination showed that most of the particulate matter was reddish brown-to-black amorphous particles a few micrometers in diameter. These were not active in polarized light. One large particle, about  $25 \times 40 \mu\text{m}$  in size, had a distinct gray metallic appearance and also had some green crystals along one surface. This could possibly be a metal chip with some acid salts on its surface. There were also some small particles, some stringy in shape, that showed some optical activity in polarized light. These might have been some fragments of plastic, such as Teflon pipe-joint tape. Some of the polyvinyl chloride filter sheets used for duct sampling appeared to have holes melted in them, with a particle embedded in the filter. Apparently, some of the particles were hot when collected. This, of course, was not observed when fibrous glass filters were used for sampling.

Since the brown-to-black particles were suspected to be iron products (some were attracted by a magnet), swatches of the filter paper were treated with 12N HCl. The dark deposit dissolved completely, leaving a yellow solution. This solution then gave a deep red color with KCNS solution, the usual test for dissolved iron. It was found that the polyvinyl chloride filter material also gave a weak test for iron by this method, not as strong as that from the particulate samples.

Photographs at increasing magnifications are shown for the particulate samples collected from one of the duct probes (Figs. 4 to 9) and from one of the steam-exhaust probes (Figs. 10 and 11). Photographs are also shown for a sample of loose debris taken from the duct during a shutdown period (Figs. 12 to 14). It is apparent from these pictures that, even at the highest powers, the particles are amorphous, suggestive of iron oxide or fluoride. The particle size ranges from hundreds of micrometers down to hundredths of a micrometer in diameter, with a preponderance of population in the respirable range around  $1 \mu\text{m}$ .



(a) 1X magnification



(b) 6X magnification

Fig. 4 - Particulate sample from near duct wall



(a) 40X magnification



(b) 200X magnification

Fig. 5 - Particulate sample from near duct wall

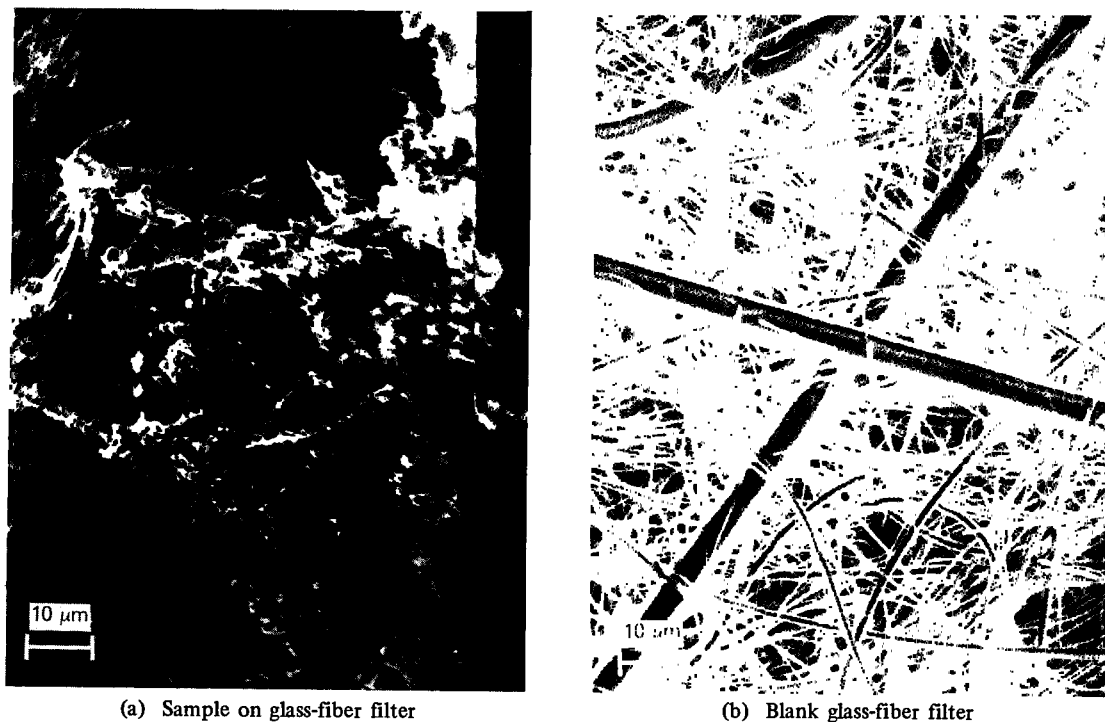


Fig. 6 — Particulate sample from near duct wall at 1000 $\times$  magnification

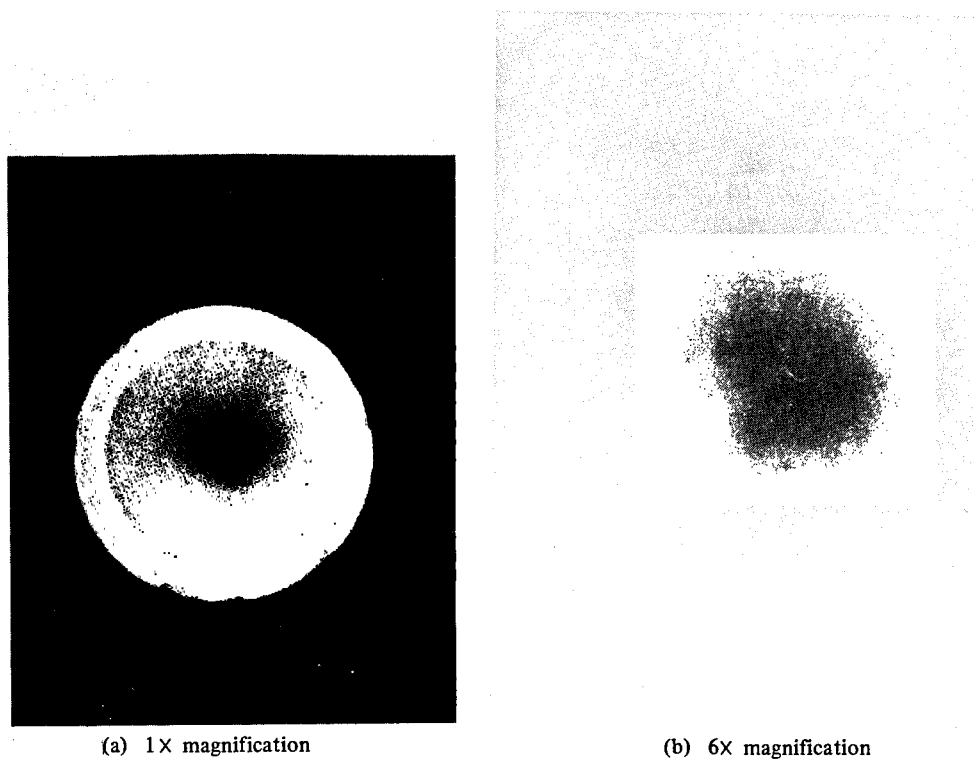


Fig. 7 — Particulate sample from near duct centerline

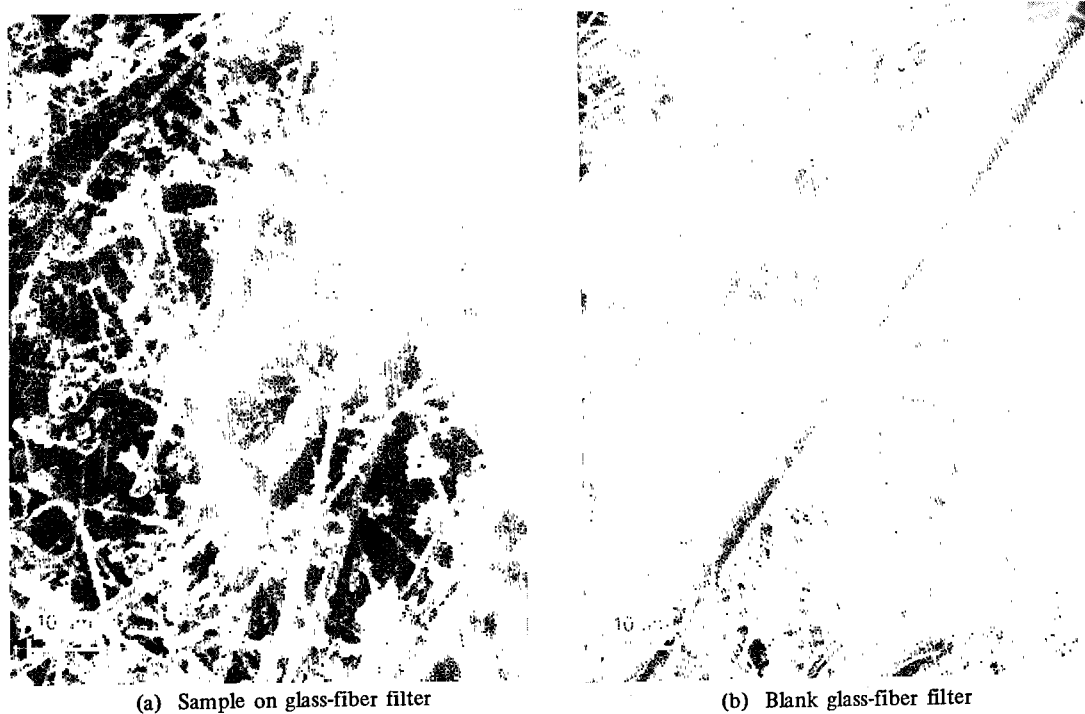


Fig. 8 – Particulate sample from near duct centerline  
at 1000X magnification:

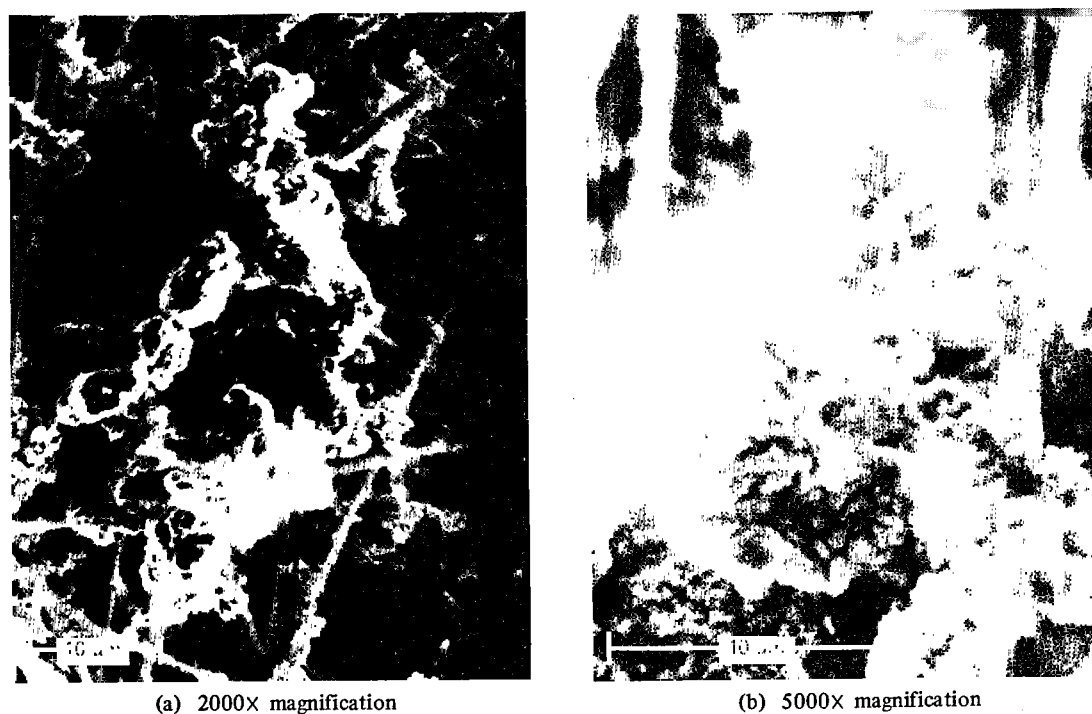
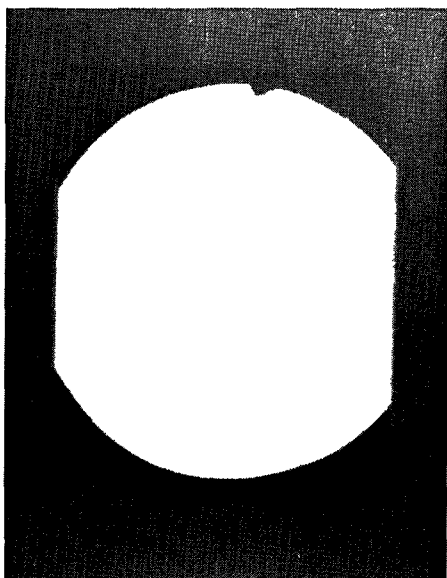


Fig. 9 – Particulate sample from near duct centerline



(a) 2X magnification

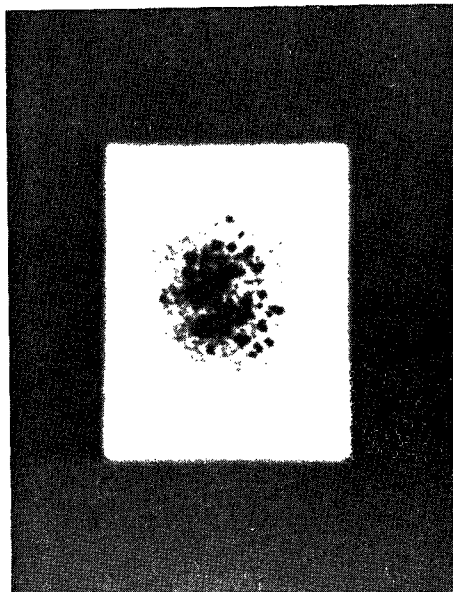


(b) 40X magnification

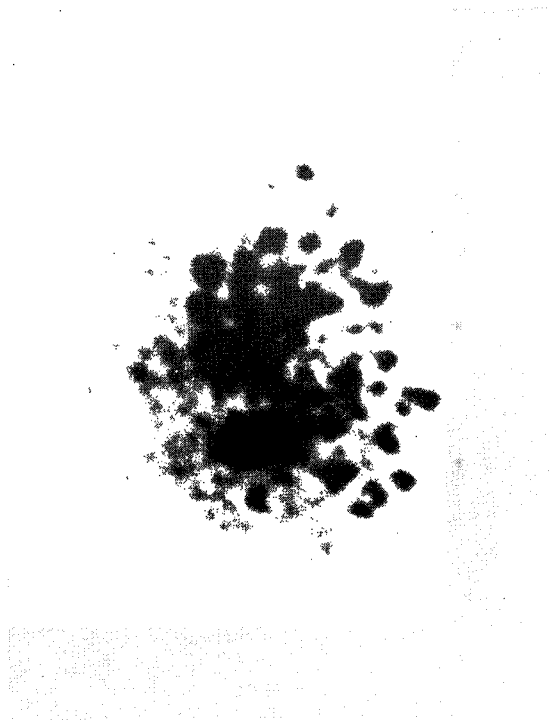
Fig. 10 – Particulate sample from duct steam exhaust



Fig. 11 – Particulate samples from steam exhaust at  
1000X magnification

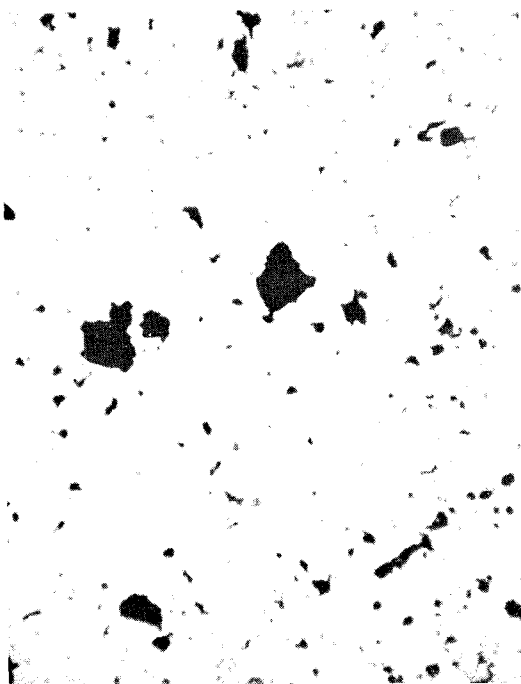


(a) 3X magnification



(b) 6X magnification

Fig. 12 - Particulate debris from inside wall of duct



(a) 40X magnification



(b) 1000X magnification

Fig. 13 - Particulate debris from inside wall of duct

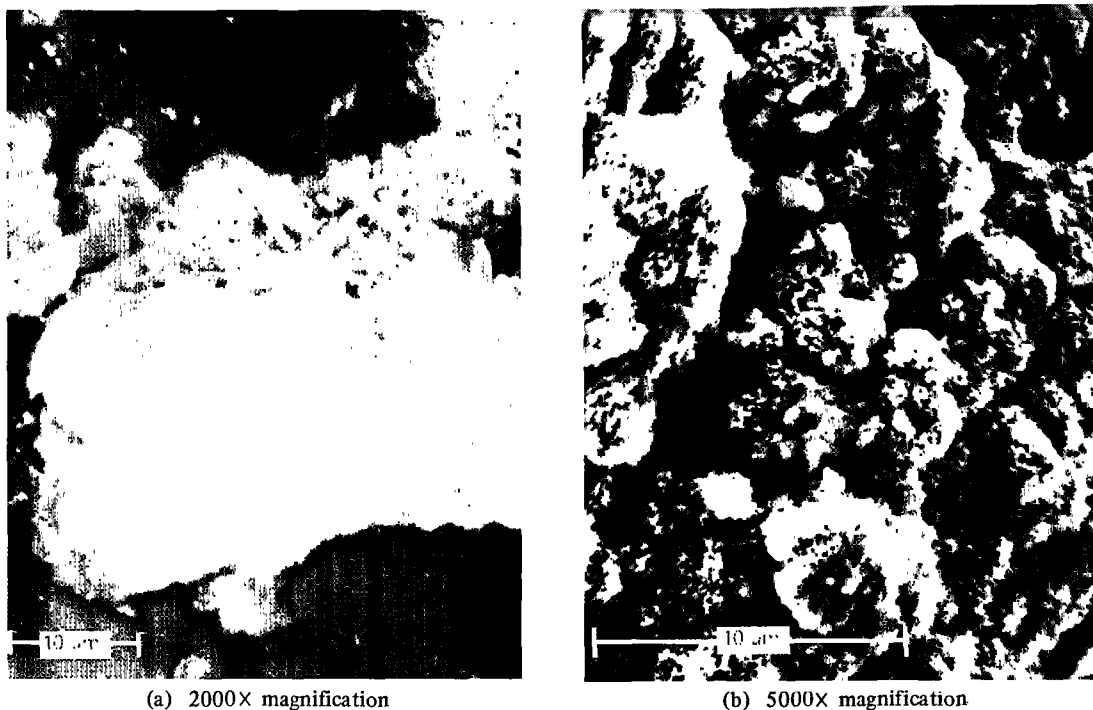


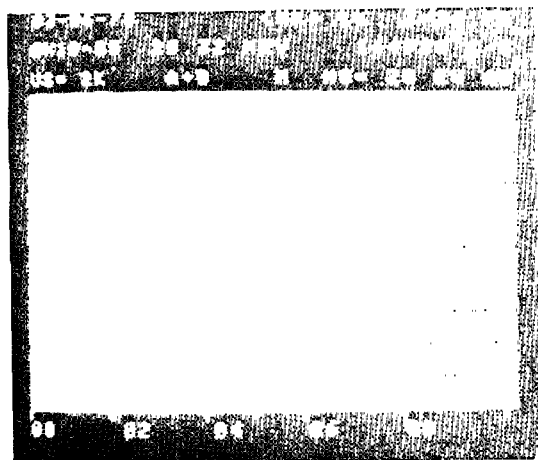
Fig. 14 – Particulate debris from inside wall of duct

An x-ray spectrographic analysis (Kevex) was made on the duct-filter sample, the duct-debris sample, and a blank piece of filter paper. These spectra are shown in Fig. 15. It is apparent from these analyses that iron is a major constituent in these particulate samples. Traces are also seen of titanium, fluorine, and the constituents of the glass filter paper itself.

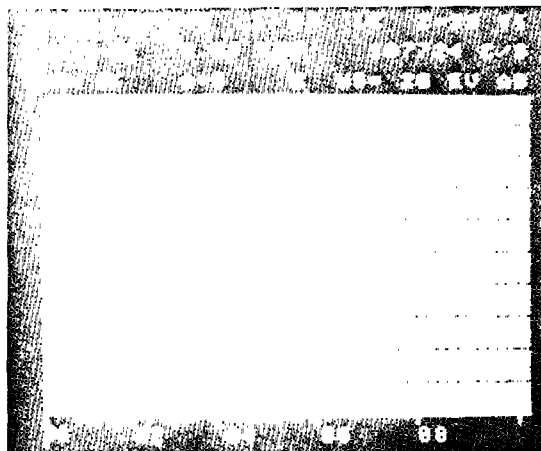
The particulate samples from the duct and from the steam exhaust were subsequently dissolved from the filter paper with aqua regia (mixed nitric and hydrochloric acids) to give reddish-brown solutions, with no residue remaining on the paper. These extracts were then analyzed colorimetrically for iron by use of the ferric thiocyanate color reaction in a photoelectric colorimeter. The volume of air sampled through the filter papers is known; hence, the concentration of iron as grams per liter of air could be calculated. Then, on the assumption that the iron was present as iron oxide with an average particle diameter of  $1\text{ }\mu\text{m}$ , a particle number concentration could be calculated. The assumption that the particulate samples consisted entirely of  $1\text{-}\mu\text{m}$ -diameter particles of ferric oxide was arbitrary for the purpose of comparative calculation. The results are shown in Table 7. If the steam-dilution factor is 6 to 1, about 84% of the particles are removed by the scrubber.

#### Analysis of Duct Debris

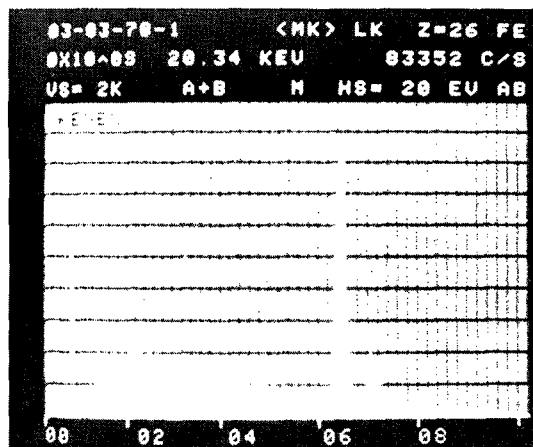
The debris collected from the wall inside the duct was a brown, amorphous dust. It was strongly attracted by a magnet held near the container wall, which indicated the presence of iron. One portion was mixed with water to give a turbid liquid suspension and a dark-brown residue. The supernatant liquid was analyzed for soluble fluoride with the specific ion meter.



(a) Blank glass-filter paper



(b) Particulate sample and filter from duct centerline probe



(c) Particulate debris from inside wall of duct

Fig. 15 - X-ray spectrographic analysis (Kevex) of particulate samples



Table 7 — Concentration of Iron and of Iron Calculated as Oxide Particles in the NACL Duct and Exhaust

Sample Location	Iron Concentration (g Fe/l air at ambient temperature and pressure)	Iron Oxide Particle Concentration (assumed 1- $\mu$ m-diameter particles/l at ambient temperature and pressure)
Duct Centerline, Long Probe	$330 \times 10^{-6}$	$5 \times 10^8$
Steam Exhaust	$8 \times 10^{-6}$	$1 \times 10^7$

The soluble-fluoride content of this liquid was 0.05% of the weight of the sample. The other portion of the duct debris was mixed with 12N HCl to give a clear red-brown solution and negligible residue. This solution also was analyzed for soluble fluoride. The fluoride content of this solution was 10% of the weight of the sample. The ratio of 0.05% to 10.0% is in direct proportion to the relative solubilities of iron fluoride in water and in HCl. Hence, one may conclude that the residue in the duct was about 10% iron fluoride and the rest iron oxide or other acid-soluble iron compounds.

## SUMMARY

Methods have been developed at NRL to sample the NACL. These include particulate and fluoride analysis, both upstream and downstream from the pump, and on-line mass-spectrometric analysis upstream from the pump. These methods have been used at the NACL and found to work well. Data from the mass-spectrometric analysis show the principal toxic gases emitted from the NACL to be HF and DF. No other toxic fluorine containing species was detected. Any other toxic material not detected would be less than 0.3% of the HF/DF concentration. The concentration of HF/DF in the pipe between the laser and the pumps was 5000 to 100,000 ppm. The concentration of HF/DF in the final exhaust after the pumps was about 10 to 15% of that in the pipe, implying little scrubbing due to pumping. The particulate matter was found to be 90% iron oxide and 10% iron fluoride. About 85% of the particulate matter is removed by the pumps. Toxicological data are available for humans exposed to high HF/DF levels for short periods of time [4,5]. Exposure to 100 ppm for less than 1 min can cause permanent damage to the human respiratory system as well as severe skin burns. Since high levels of HF/DF were measured in the NACL exhaust, serious consideration should be given to monitoring of HF/DF in the vicinity of the NACL after firing.

The requirements of the National Environmental Policy Act (NEPA), insofar as Navy compliance is concerned, are detailed in Refs. 6 to 9. NEPA requires the Navy to submit Environmental Impact Assessments/Statements for shipboard installations, supporting storage, and R&D test facilities. R&D test facilities do not, at this time, have any exemption from

NEPA, and their activities can be restricted by EPA. Updating of environmental assessments must be made on a continuing basis to reflect changes in design and chemical reactant selection. The results of this study can be used as a guideline for the design goals of future "chemical scrubbing" systems and as a baseline when compared with the chemical exhaust of newer laser systems.

## RECOMMENDATIONS FOR FURTHER WORK

This section describes three areas where additional research and development efforts would be beneficial. These recommendations are based on the results of this report and on experience at the TRW site. Areas for future study are: development of instrumental methods for gas monitoring, evaluation of exhaust particulate hazards as the scrubbing system changes, and characterization of  $\text{NF}_3$  combustion and combustion control. These areas are outlined below.

### Gas Monitoring

The results of this study have shown that hydrogen and deuterium fluoride ( $\text{HF}/\text{DF}$ ) and carbon tetrafluoride ( $\text{CF}_4$ ) are the only significant fluorine-bearing compounds in the NACL exhaust.

The present U.S. Occupational Standard for exposure to HF is a time-weighted average (TWA) of 3 ppm. The TWA for  $\text{CF}_4$  has yet to be established; however, it would be expected to be high. The exhaust analysis reported in this study indicates that  $\text{NF}_3$  is not in the exhaust, because it is completely consumed during the NACL operation. However, since large quantities of  $\text{NF}_3$  must be stored, a potential safety hazard exists. The U.S. Occupational Standard for  $\text{NF}_3$  is a TWA in air of 10 ppm. Besides the personnel-exposure hazards of HF and  $\text{NF}_3$ , two additional problems exist: (1) HF is highly corrosive and its presence would damage electronic and optical equipment; (2)  $\text{NF}_3$  can, under certain conditions, spontaneously ignite when in contact with most materials.

### *Objective and Approach*

We recommend the development of an instrumental method to monitor continuously for  $\text{NF}_3$  and HF. Based on our experiences with the detection of NACL exhaust gases, we believe mass spectrometry should be one of the primary approaches investigated. Currently, a prototype of a second-generation central-atmosphere monitor (CAMS-II) for submarine use is being developed. A modified CAMS-II, incorporating different software and sampling system, might be the instrument to meet the objective. As a backup, a NASA chemiluminescence detector and other optical methods should undergo feasibility studies. The chemiluminescence detector is designed for HCl detection; however, the method might be modified to detect  $\text{NF}_3$  and/or HF. An optical method such as correlation infrared could yield an instrument with high specificity, although a slow response time may present complications. In all areas of investigation, sensitivity, response time, and specificity should be determined.

## Particulate Studies

The results of this study show significant concentrations of iron-containing particles (iron oxide and iron fluoride) in the duct and exhaust gases of the NACL system. The concentration of these particles in the vicinity of the NACL during and immediately after firing pose a health hazard.

### *Objective and Approach*

The objective of this study is to assess the respiratory hazard as changes are made in the scrubbing system, as well as any material changes in exhaust ducts. Inertial methods such as cascade impactors can be used to collect particulate samples by particle size. On the basis of particle size analysis and chemical nature of the material, an evaluation can be made as to how much of the exhausted material represents a respiratory hazard. By monitoring the NACL effluent one can determine the efficiency of scrubbing or other cleaning methods.

## NF<sub>3</sub> Combustion

Nitrogen trifluoride can ignite and burn with a large number of fuels and materials. To assess the toxic hazard of an NF<sub>3</sub> fire, chemicals produced during NF<sub>3</sub> combustion must be known. In addition, the concentration of the fire-suppressing agent Halon 1301 (CF<sub>3</sub>Br) at which an NF<sub>3</sub> fire is extinguished and what new products are produced by its use should be determined.

### *Objective and Approach*

A study of a controlled NF<sub>3</sub> burner fire in an enclosed fire chamber should be undertaken. The NF<sub>3</sub> burner fire should use C<sub>2</sub>H<sub>4</sub> as a fuel or any other fuel proposed to be used in NACL. The chemical products of this fire can be analyzed on-line with a mass spectrometer. In addition, Halon 1301 should be introduced into the chamber until the NF<sub>3</sub> fire is extinguished. The concentration of Halon 1301 should be constantly monitored. Any other products formed upon addition of Halon 1301 should be ascertained.

## ACKNOWLEDGMENTS

The authors thank Dr. R. A. DeMarco for the synthesis of several fluorine-containing compounds used in this study, and they thank Dr. W. B. Fox for his continuing advice and encouragement.

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**Appendix**  
**MASS SPECTRA FOR RUNS VL2-170 AND VL2-171**

The tables in this appendix list the actual mass spectra obtained for runs VL2-170 (morning run) and VL2-171 (afternoon run). The mass for each row is given in Column 1. Columns represent a given spectrum. Thus, by scanning across a row one observes the intensity of a mass as a function of time during a run. The time for each spectrum is given in Table 1. Examples of the interpretation of the data are presented in the text.

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Run VL2-170: 9/12/77 morning Part 1

m/e	Intensities							
2	41.16	394.04	440.19	458.25	505.13	569.82	596.44	455.57
3	0.11	0.63	183.59	202.39	229.00	301.51	319.58	208.01
4	10.00	4013.67	3347.17	3945.31	3845.21	4880.37	4840.63	2714.84
16	10.00	22.58	31.91	40.19	35.42	31.88	29.76	26.17
17	14.43	133.06	289.55	324.95	249.51	183.84	139.89	109.62
18	53.08	525.63	1220.70	1257.32	961.91	682.37	525.15	401.37
19	0.21	3.64	38.53	140.63	199.71	210.69	210.21	162.11
20	2.03	3.35	9.03	12.33	23.17	34.01	40.67	37.28
21	0.02	0.06	0.31	0.37	0.95	1.44	2.19	1.58
25	0.30	0.78	0.74	0.77	0.70	1.16	1.10	0.63
26	1.42	1.47	1.15	1.24	1.49	1.74	2.04	1.48
27	10.00	6.54	5.93	5.49	5.91	7.57	7.50	6.23
28	2661.13	755.37	682.13	738.77	722.90	925.29	964.36	684.08
29	5.47	6.49	6.32	6.37	6.49	7.10	7.52	6.64
30	0.84	1.66	1.44	1.82	1.98	2.21	2.44	1.83
31	0.53	2.59	2.27	2.71	2.58	3.09	3.36	1.76
32	26.22	10.00	2.53	1.88	1.58	1.47	1.23	2.99
33	0.07	8.43	0.17	0.18	0.24	0.17	0.13	0.13
34	0.35	0.28	0.17	0.13	0.19	0.18	0.28	0.24
35	0.18	0.14	0.25	0.20	0.27	0.24	0.33	0.31
36	0.39	0.48	0.60	0.60	0.59	0.84	0.74	0.80
37	0.01	0.15	0.30	0.20	0.31	0.37	0.43	0.24
38	0.22	0.24	0.39	0.28	0.42	0.37	0.46	0.46
39	0.47	0.49	0.36	0.38	0.46	0.51	0.61	0.35
40	11.33	18.58	18.65	16.82	19.51	21.09	24.95	22.09

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Run VL2-170: 9/12/77 morning Part 2

m/e	Intensities								
41	0.13	0.24	0.27	0.21	0.16	0.28	0.26	0.19	
42	0.19	0.18	0.13	0.23	0.13	0.25	0.24	0.22	
43	0.12	0.22	0.17	0.23	0.22	0.38	0.37	0.17	
44	6.31	8.89	7.86	9.45	12.04	11.87	11.40	8.94	
45	0.17	0.15	0.14	0.27	0.24	0.21	0.07	0.10	
46	0.00	0.04	0.05	0.14	0.26	0.22	0.02	0.14	
47	0.14	0.20	0.01	0.18	0.18	0.20	0.01	0.10	
48	0.06	0.00	0.03	0.12	0.15	0.11	0.07	0.09	
49	0.11	0.14	0.15	0.19	0.21	0.15	0.23	0.04	
50	0.00	6.75	7.01	6.45	7.20	8.13	8.62	5.59	
51	0.10	0.31	0.06	0.10	0.10	0.11	0.05	0.15	
52	0.03	26.81	0.40	0.34	0.13	0.21	0.15	0.15	
53	0.00	0.04	0.07	0.07	0.05	0.04	0.08	0.18	
54	0.02	0.01	0.05	0.07	0.08	0.06	0.14	0.07	
55	0.06	0.04	0.06	0.12	0.06	0.08	0.05	0.19	
56	0.01	0.00	0.03	0.10	0.09	0.07	0.12	0.15	
57	0.00	0.00	0.03	0.03	0.00	0.05	0.09	0.15	
58	0.01	0.08	0.13	0.10	0.05	0.02	0.12	0.03	
59	0.01	0.00	0.07	0.09	0.00	0.06	0.01	0.06	
60	0.05	0.02	0.03	0.10	0.02	0.04	0.07	0.02	
61	0.00	0.00	0.04	0.08	0.05	0.03	0.05	0.05	
62	0.00	0.00	0.06	0.08	0.01	0.07	0.06	0.01	
63	0.08	0.06	0.12	0.16	0.04	0.00	0.06	0.00	
64	0.11	0.10	0.10	0.09	0.00	0.04	0.09	0.00	
65	0.09	0.08	0.13	0.15	0.03	0.01	0.21	0.00	

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Run VL2-170: 9/12/77 morning Part 3

m/e	Intensities							
66	0.04	0.14	0.22	0.11	0.16	0.18	0.20	0.05
67	0.11	0.27	0.21	0.34	0.21	0.31	0.32	0.13
68	0.05	1.28	1.02	1.11	0.94	1.33	0.99	0.58
69	0.05	10.00	51.46	52.47	57.20	65.06	69.63	45.65
70	0.11	10.00	0.56	0.73	0.64	0.56	0.80	0.29
71	0.02	6.71	0.12	0.16	0.07	0.05	0.02	0.00
72	0.08	0.17	0.03	0.08	0.11	0.02	0.04	0.06
73	0.00	0.11	0.03	0.08	0.00	0.06	0.00	0.00
74	0.00	0.13	0.03	0.05	0.07	0.02	0.00	0.00
75	0.00	0.05	0.00	0.09	0.11	0.05	0.00	0.17
76	0.00	0.12	0.02	0.06	0.03	0.02	0.00	0.00
77	0.00	0.05	0.07	0.18	0.19	0.17	0.10	0.09
78	0.00	0.08	0.02	0.02	0.07	0.14	0.00	0.00
79	0.05	0.06	0.06	0.07	0.04	0.11	0.12	0.16
80	0.00	0.03	0.04	0.07	0.01	0.11	0.07	0.00
81	0.00	0.10	0.04	0.13	0.06	0.10	0.13	0.00
82	0.00	0.05	0.05	0.00	0.03	0.06	0.07	0.00
83	0.00	0.05	0.05	0.00	0.00	0.10	0.05	0.00
84	0.00	0.07	0.00	0.02	0.02	0.23	0.21	0.00
85	0.09	0.11	0.09	0.05	0.07	0.59	0.49	0.00
86	0.11	0.09	0.16	0.01	0.00	0.08	0.10	0.00
87	0.09	0.09	0.04	0.00	0.03	0.00	0.06	0.00
88	0.00	0.02	0.03	0.01	0.00	0.00	0.02	0.00
89	0.06	0.11	0.00	0.03	0.02	0.00	0.08	0.00
90	0.07	0.06	0.05	0.04	0.00	0.00	0.01	0.00



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Run VL2-170: 9/12/77 morning Part 4

m/e	Intensities									
91	0.11	0.00	0.07	0.05	0.03	0.05	0.04	0.00		
92	0.00	0.00	0.01	0.06	0.00	0.07	0.08	0.00		
93	0.06	0.00	0.04	0.04	0.01	0.06	0.06	0.00		
94	0.05	0.00	0.10	0.00	0.04	0.12	0.00	0.00		
95	0.00	0.00	0.01	0.02	0.08	0.19	0.00	0.00		
96	0.00	0.00	0.11	0.05	0.08	0.12	0.00	0.00		
97	0.00	0.00	0.03	0.02	0.11	0.09	0.00	0.00		
98	0.03	0.00	0.01	0.05	0.02	0.21	0.06	0.00		
99	0.00	0.05	0.01	0.02	0.13	0.15	0.01	0.00		
100	0.00	0.03	0.00	0.00	0.01	0.16	0.04	0.00		
101	0.00	0.05	0.00	0.05	0.06	0.09	0.02	0.00		
102	0.00	0.03	0.00	0.00	0.04	0.11	0.05	0.00		
103	0.00	0.02	0.00	0.07	0.10	0.16	0.00	0.00		
104	0.00	0.08	0.03	0.07	0.01	0.10	0.00	0.00		
105	0.00	0.10	0.03	0.11	0.04	0.13	0.00	0.00		
106	0.00	0.04	0.00	0.08	0.05	0.03	0.09	0.00		
107	0.05	0.10	0.00	0.07	0.04	0.05	0.00	0.00		
108	0.05	0.13	0.01	0.12	0.00	0.09	0.01	0.00		
109	0.04	0.13	0.01	0.08	0.03	0.03	0.06	0.00		
110	0.01	0.23	0.00	0.14	0.04	0.10	0.11	0.00		
111	0.07	0.09	0.00	0.09	0.00	0.00	0.10	0.00		
112	0.00	0.09	0.00	0.10	0.00	0.05	0.12	0.00		
113	0.09	0.13	0.01	0.10	0.02	0.03	0.11	0.00		
114	0.03	0.10	0.10	0.06	0.01	0.12	0.08	0.00		
115	0.06	0.04	0.00	0.09	0.12	0.02	0.01	0.00		

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Run VL2-170: 9/12/77 morning Part 5

m/e	Intensities											
116	0.02	0.20	0.05	0.07	0.00	0.03	0.15	0.00				
117	0.01	0.08	0.08	0.08	0.07	0.08	0.06	0.00				
118	0.09	0.23	0.03	0.06	0.11	0.12	0.06	0.00				
119	0.00	0.14	0.00	0.11	0.00	0.06	0.00	0.00				
120	0.10	0.10	0.07	0.12	0.06	0.01	0.09	0.00				
121	0.00	0.11	0.03	0.05	0.01	0.00	0.03	0.00				
122	0.01	0.13	0.03	0.10	0.06	0.11	0.08	0.00				
123	0.05	0.08	0.01	0.16	0.09	0.02	0.03	0.00				
124	0.00	0.12	0.00	0.06	0.05	0.02	0.03	0.00				
125	0.11	0.04	0.01	0.05	0.05	0.10	0.01	0.00				
126	0.13	0.04	0.00	0.10	0.11	0.05	0.10	0.00				
127	0.11	0.00	0.00	0.08	0.09	0.03	0.10	0.00				
128	0.07	0.03	0.00	0.02	0.03	0.00	0.13	0.00				
129	0.18	0.12	0.03	0.04	0.06	0.00	0.06	0.00				
130	0.00	0.09	0.00	0.00	0.10	0.06	0.07	0.00				
131	0.12	0.02	0.10	0.05	0.07	0.05	0.00	0.00				
132	0.05	0.10	0.00	0.08	0.07	0.00	0.06	0.00				
133	0.05	0.09	0.06	0.07	0.05	0.01	0.07	0.00				
134	0.11	0.00	0.01	0.04	0.07	0.06	0.08	0.00				
135	0.00	0.10	0.07	0.06	0.06	0.00	0.11	0.00				
136	0.16	0.03	0.05	0.03	0.03	0.03	0.00	0.00				
137	0.10	0.00	0.01	0.00	0.06	0.02	0.03	0.00				
138	0.04	0.03	0.09	0.03	0.10	0.02	0.00	0.00				
139	0.17	0.04	0.07	0.00	0.04	0.08	0.00	0.00				
140	0.06	0.03	0.14	0.01	0.09	0.01	0.05	0.00				

## DeCORPO, CLARK, THOMPSON, HUDGENS, OLFKY, AND WYATT

Run VL2-170: 9/12/77 morning Part 6

m/e	Intensities							
141	0.22	0.05	0.11	0.00	0.02	0.10	0.02	0.00
142	0.09	0.05	0.11	0.03	0.07	0.02	0.00	0.00
143	0.12	0.10	0.05	0.02	0.08	0.10	0.00	0.00
144	0.00	0.08	0.11	0.00	0.03	0.02	0.00	0.00
145	0.11	0.11	0.06	0.08	0.04	0.00	0.00	0.00
146	0.00	0.03	0.12	0.00	0.00	0.02	0.04	0.00
147	0.02	0.09	0.07	0.07	0.03	0.00	0.00	0.00
148	0.18	0.06	0.00	0.04	0.00	0.01	0.03	0.00
149	0.01	0.06	0.06	0.08	0.00	0.00	0.08	0.00
150	0.02	0.00	0.12	0.04	0.08	0.02	0.00	0.00

## NRL REPORT 8273

Run VL2-171: 9/12/77 afternoon Part 1

m/e	Intensities					
2	63.06	615.97	1096.19	1123.05	1237.79	854.49
3	2.55	2.84	5.52	593.51	662.11	382.32
4	5.71	3820.80	12451.17	9887.70	11572.27	6042.48
16	6.23	45.63	42.24	64.36	73.66	52.00
17	15.01	209.47	243.90	596.68	517.09	309.08
18	55.20	814.45	1015.63	2448.73	1999.51	1164.55
19	1.11	8.20	19.65	298.58	416.75	286.87
20	4.58	5.49	10.06	31.27	46.63	48.73
21	0.02	0.13	0.09	1.12	1.48	1.35
25	0.66	0.38	3.06	2.34	2.38	1.12
26	3.36	2.06	2.74	2.60	2.90	2.04
27	5.76	17.36	8.98	11.79	11.87	10.72
28	6999.51	3000.49	2248.54	1806.64	2021.48	1403.81
29	11.21	30.93	13.48	15.31	16.63	13.23
30	2.15	2.36	5.03	6.98	7.64	5.96
31	1.63	0.53	9.87	7.79	8.52	5.25
32	77.34	81.79	10.00	5.00	3.11	9.38
33	0.26	0.14	77.25	0.49	0.54	0.32
34	0.88	0.38	0.57	0.25	0.36	0.26
35	0.12	0.21	0.32	0.23	0.38	0.21
36	0.65	0.68	0.86	1.09	1.05	0.99
37	0.07	0.12	0.30	0.34	0.52	0.30
38	0.31	0.25	0.69	0.65	0.60	0.46
39	1.00	0.58	0.87	0.99	0.98	0.64
40	25.34	56.47	40.75	45.83	47.85	39.70

## DeCORPO, CLARK, THOMPSON, HUDGENS, OLFKY, AND WYATT

Run VL2-171: 9/12/77 afternoon Part 2

m/e	Intensities					
41	0.26	0.33	0.55	0.48	0.62	0.39
42	0.18	0.24	0.45	0.35	0.44	0.32
43	0.14	0.25	0.54	0.41	0.57	0.41
44	4.98	9.64	12.11	14.28	17.46	14.21
45	0.07	0.10	0.36	0.26	0.32	0.24
46	0.00	0.10	0.24	0.20	0.21	0.12
47	0.00	0.08	0.45	0.25	0.23	0.08
48	0.11	0.21	0.19	0.19	0.12	0.09
49	0.05	0.06	0.38	0.32	0.31	0.07
50	0.01	0.20	10.00	19.29	22.12	12.65
51	0.00	0.13	10.00	0.41	0.35	0.15
52	0.00	0.17	40.77	1.07	0.70	0.75
53	0.04	0.02	0.16	0.04	0.10	0.13
54	0.06	0.00	0.13	0.05	0.11	0.07
55	0.01	0.10	0.14	0.13	0.10	0.17
56	0.00	0.07	0.05	0.12	0.19	0.15
57	0.00	0.00	0.09	0.12	0.04	0.02
58	0.04	0.02	0.07	0.15	0.11	0.16
59	0.00	0.07	0.05	0.07	0.06	0.07
60	0.00	0.03	0.11	0.15	0.05	0.10
61	0.00	0.10	0.08	0.05	0.12	0.13
62	0.10	0.09	0.10	0.10	0.10	0.13
63	0.00	0.03	0.10	0.08	0.10	0.10
64	0.30	0.00	0.24	0.29	0.13	0.11
65	0.00	0.11	0.26	0.29	0.16	0.04

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Run VL2-171: 9/12/77 afternoon Part 3

m/e	Intensities					
66	0.07	0.00	0.57	0.52	0.41	0.12
67	0.00	0.06	1.03	0.64	0.70	0.26
68	0.00	0.00	0.92	0.75	0.70	0.35
69	0.00	0.06	42.97	194.09	210.94	93.02
70	0.00	0.00	2.40	1.82	2.10	0.63
71	0.02	0.00	36.04	0.39	0.23	0.14
72	0.10	0.02	0.11	0.08	0.10	0.13
73	0.10	0.02	0.14	0.10	0.12	0.01
74	0.00	0.06	0.12	0.08	0.09	0.13
75	0.00	0.00	0.15	0.10	0.06	0.00
76	0.00	0.04	0.10	0.08	0.16	0.09
77	0.10	0.00	0.09	0.11	0.22	0.12
78	0.10	0.06	0.10	0.09	0.17	0.10
79	0.12	0.00	0.06	0.11	0.11	0.08
80	0.00	0.05	0.14	0.02	0.07	0.11
81	0.06	0.10	0.09	0.07	0.16	0.24
82	0.00	0.14	0.09	0.04	0.12	0.06
83	0.09	0.00	0.18	0.03	0.16	0.05
84	0.00	0.00	0.10	0.11	0.03	0.03
85	0.04	0.03	0.11	0.11	0.09	0.36
86	0.06	0.00	0.11	0.12	0.03	0.12
87	0.13	0.03	0.13	0.17	0.10	0.16
88	0.03	0.09	0.19	0.09	0.07	0.15
89	0.00	0.07	0.12	0.09	0.05	0.03
90	0.00	0.20	0.19	0.08	0.10	0.16

DeCORO, CLARK, THOMPSON, HUDDGENS, OLFKY, AND WYATT

Run VL2-171: 9/12/77 afternoon Part 4

m/e	Intensities							
91	0.03	0.01	0.09	0.11	0.02	0.05		
92	0.08	0.21	0.07	0.09	0.14	0.14		
93	0.04	0.06	0.06	0.04	0.05	0.00		
94	0.00	0.03	0.07	0.04	0.09	0.17		
95	0.00	0.09	0.15	0.04	0.02	0.11		
96	0.09	0.12	0.13	0.05	0.11	0.15		
97	0.00	0.07	0.16	0.12	0.02	0.00		
98	0.00	0.19	0.12	0.14	0.09	0.00		
99	0.00	0.14	0.19	0.10	0.04	0.03		
100	0.07	0.15	0.15	0.08	0.15	0.10		
101	0.05	0.08	0.06	0.06	0.12	0.06		
102	0.06	0.16	0.12	0.03	0.10	0.10		
103	0.02	0.14	0.08	0.10	0.09	0.07		
104	0.00	0.06	0.12	0.10	0.14	0.00		
105	0.00	0.05	0.14	0.10	0.10	0.03		
106	0.00	0.00	0.19	0.13	0.15	0.00		
107	0.07	0.09	0.09	0.04	0.10	0.02		
108	0.08	0.07	0.07	0.10	0.12	0.00		
109	0.00	0.12	0.08	0.00	0.12	0.10		
110	0.00	0.08	0.11	0.09	0.12	0.01		
111	0.00	0.05	0.14	0.00	0.15	0.04		
112	0.03	0.00	0.06	0.16	0.13	0.00		
113	0.00	0.06	0.14	0.08	0.12	0.00		
114	0.05	0.04	0.17	0.12	0.10	0.00		
115	0.00	0.10	0.13	0.10	0.10	0.07		

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Run VL2-171: 9/12/77 afternoon Part 5

m/e	Intensities					
116	0.00	0.07	0.07	0.13	0.10	0.07
117	0.07	0.00	0.09	0.10	0.10	0.03
118	0.00	0.04	0.03	0.13	0.15	0.03
119	0.00	0.13	0.07	0.06	0.18	0.06
120	0.00	0.19	0.02	0.04	0.16	0.12
121	0.03	0.08	0.11	0.12	0.15	0.17
122	0.00	0.01	0.07	0.13	0.08	0.00
123	0.17	0.12	0.12	0.00	0.10	0.13
124	0.01	0.02	0.04	0.17	0.12	0.10
125	0.00	0.17	0.03	0.11	0.20	0.18
126	0.00	0.10	0.06	0.12	0.10	0.15
127	0.00	0.06	0.21	0.08	0.13	0.11
128	0.03	0.15	0.14	0.04	0.08	0.16
129	0.07	0.00	0.12	0.10	0.03	0.03
130	0.00	0.01	0.14	0.10	0.14	0.11
131	0.06	0.08	0.21	0.03	0.10	0.05
132	0.10	0.07	0.09	0.00	0.14	0.11
133	0.14	0.14	0.13	0.08	0.15	0.07
134	0.06	0.00	0.00	0.17	0.14	0.09
135	0.02	0.09	0.16	0.06	0.10	0.13
136	0.02	0.01	0.08	0.14	0.11	0.12
137	0.03	0.00	0.08	0.03	0.13	0.05
138	0.01	0.04	0.06	0.11	0.21	0.10
139	0.00	0.13	0.11	0.08	0.12	0.02
140	0.03	0.16	0.06	0.04	0.05	0.04



## DeCORPO, CLARK, THOMPSON, HUDGENS, OLFKY, AND WYATT

Run VL2-171: 9/12/77 afternoon Part 6

m/e	Intensities					
141	0.00	0.12	0.00	0.06	0.12	0.00
142	0.00	0.05	0.03	0.00	0.14	0.03
143	0.02	0.00	0.13	0.02	0.07	0.00
144	0.06	0.06	0.15	0.10	0.06	0.10
145	0.03	0.04	0.21	0.01	0.03	0.06
146	0.03	0.06	0.13	0.13	0.04	0.09
147	0.00	0.00	0.07	0.15	0.07	0.00
148	0.00	0.05	0.10	0.12	0.14	0.09
149	0.01	0.02	0.16	0.20	0.11	0.03
150	0.03	0.03	0.14	0.07	0.07	0.19